

## THERMOCHEMICAL MODULE FOR HYDROGEN PRODUCTION BY STEAM REFORMING OF METHANOL

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Vehicles, the significant portion of which come in the form of automobiles and tractors, are referred to as basic sources of commercial air pollution [1]. Two means of lowering the level of atmospheric emissions are currently being considered: modification of existing working processes in internal combustion engines without significant changes in design [2], and conversion to a principally new conceptual vehicle design – the creation of electric automobiles with an on-board source of electric power, which runs on the base of a proton-exchange fuel cell [3]. In both cases, we are speaking of on-board distribution of an autonomous source of hydrogen for automobiles. Since means discussed for the storage of a hydrogen reserve for vehicles have been acknowledged to be inexpedient [4], investigation of the feasibility of direct on-board production of hydrogen during vehicle operation has become urgent.

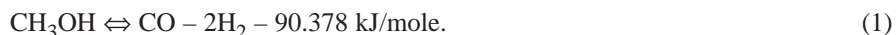
The aim of this paper was to search for a usable raw-material resource for catalytic conversion in a thermochemical module to produce hydrogen, and to study the feasibility of implementing the process of the steam reforming of the lower alcohols over a copper–chromium–zinc oxide composition applied to a zeolite carrier.

It is reasonable to suggest lightweight homologs of saturated hydrocarbons (alcans), lower alcohols, and simple ethers as a potential source of hydrogen. Selection of the primary fuel for on-board hydrogen generation is a compromise that takes into account the energy value of the fuel, the temperature conditions of the refining process, the spectrum of gases formed during reforming, and cost (Table 1) [3].

Considering the low energy capacity of the steam reforming of methanol, one may conclude that it is second after methane as a source inexpensive hydrogen. The temperature of steam-and-water reforming is an important attribute separating methanol from ethanol. Methanol is a highly adaptive raw material for the production of hydrogen.

The production of hydrogen from methane is possible by three means: decomposition, partial oxidation, and steam reforming. Let us dwell on the first and last means of extraction.

Oxides of transition metals (Ni, Pd, Cu) on a backing with a highly developed surface (for example, zeolite) are used primarily for the decomposition of methanol. Chlorides of transition metals, the content of which in the backing usually does not exceed 1% (by weight), may be used as catalysts, moreover, in this reaction [5]. The decomposition proceeds in conformity with the equation



Reaction (1) is endothermic, and takes place at 400–600°C and under atmospheric pressure.

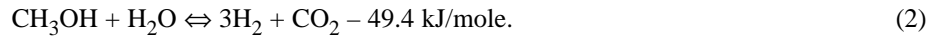
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TABLE 1

Raw material	Cost per 1 kg, dollar	Specific heat of combustion, kJ/g	Reforming temperature, K	Content in mixture, %	
				H <sub>2</sub>	CO
Methane	0.05–0.10	–50.1	1000	76.0	17.3
Propane	0.40–0.80	–46.5	700	74.0	7.2
Butane	–	–45.7	700	74.0	9.3
Octane	0.60–0.80	–44.7	>1000	70.8	20.4
Methanol	0.15–0.25	–19.7	533	74.4	4.3
Ethanol	0.20–0.30	–26.8	600	73.2	4.3
Dimethyl ether	–	–28.8	533	74.4	4.2

The production of hydrogen by the steam reforming of methanol is best understood over such metallic catalysts as copper, nickel, palladium, platinum, and rhodium [6]:



The reaction is endothermic, but the need to produce steam renders the process even more energy-consuming. Reaction (2) takes place with a good hydrogen output at a temperature of the order of 270–350°C [7].

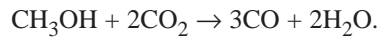
**Thermodynamic Aspects of Alcohol-Reforming.** According to published data [8], the most thermodynamically probable products of methanol reforming are hydrogen, carbon, carbon monoxide, and carbon dioxide, as well as methane. Lukyanchikov and Stezhenskii [9] present the process of thermodynamic dissociation in the simplified form:



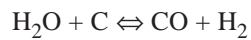
with consideration of the fact that in the methanol, there is a certain amount of water, which transforms this process into the steam reforming of the methanol in this manner, and the latter is supplemented by the conversion reaction of the water vapor:



The following reaction, which makes up for a water deficiency in the system, is also possible between the production of reactions (3) and (4):



With a sufficient amount of water, and the existence of carbon black, its decomposition



is possible.

A zinc–copper oxide catalyst (ZnO–CuO) with a ZnO content of 70–80% (remainder being CuO) ensures maximum activity with respect to methanol decomposition. Decomposition attains 65% [10, 11]. Maximum activity of the zinc–chromium catalyst corresponds to a zinc content of 75% (for both the synthesis, and decomposition of methanol). These catalysts accelerate the formation of methyl formate to the maximum extent possible, and also form, in order exceeding the amount of methane, a certain amount of formaldehyde and carbon dioxide as by-products.

Zinc–chromium–copper catalysts exhibit a higher activity, but are more sensitive to catalytic poisons (especially to sulfur compounds). They irreversibly disable iron pentacarbonyl  $\text{Fe}(\text{CO})_5$ , which forms when carbon monoxide comes in

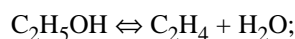
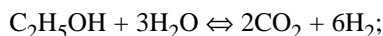
contact with the steel components of chemical vessels [12]. If, however, a high-alloy stainless steel is used as a basic structural material for the reactor, the probability of iron pentacarbonyl formation will be minimal.

In recent years, it has been discovered that many substances, for example, zeolites, which have been heretofore used as a matrix for a catalyst carrier, also exhibit catalytic properties, activity, and selectivity with respect to certain processes [13–15].

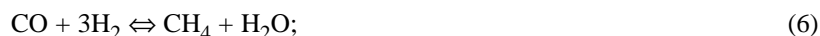
**Thermodynamic Analysis of Alcohol-Reforming Products.** Compositions of the initial effective body, which were in thermodynamic equilibrium, were analyzed to evaluate and compare initially the compositions of the products of the thermal or thermocatalytic dissociation of alcohols. The analyses were performed using standard software, libraries, and databases of the applied Chet package developed by the Institute of Air Transport, Russian Academy of Sciences.

According to a review of the literature, the analysis had to be conducted in conformity with the following mechanisms:

for ethanol



for methanol



All analyses were performed at atmospheric pressure (0.1 MPa) and at 100 K intervals within the temperature range from 400 to 1000 K. As broad a temperature range as possible was employed to ascertain the asymptotics of the development of processes taking place in the effective body, as well as to predict results of catalyst activity.

Analyses for the methanol indicated that hydrogen is manifested in the composition of the effective body at temperatures above 600 K. As the temperature increases, its content increases monotonically without sharp fluctuations. The output of hydrogen increases negligibly in the case of more dilute mixtures.

Carbon dioxide, the content of which is maximum at 800 K, is present in the composition of the effective body. Dilution with water increases its content in the system, simultaneously lowering the content of carbon monoxide, which appears after 700 K.

Maximum methane content in the composition of the effective body corresponds to the temperature level of 500–600 K, and methane disappears from the equilibrium products as the temperature increases. Dilution with water leads to a reduction in methane content. The existence of methane suggests the potential energy value of the reaction products.

A significant content of water vapor in the effective body is observed over the entire temperature interval; this is natural, since highly diluted solutions were analyzed.

Thermodynamic analyses for the ethanol yield results similar to those for the methanol. Essentially no acetaldehyde and ethylene formed under these conditions.

Further experimental investigation of the steam reforming of methanol in a carbon-free domain indicated that for the catalyst in question, no methane is formed in the composition of the reaction products, and this enables us to eliminate

TABLE 2

Volume ratio of water to alcohol	Temperature, K	Ratio of amount of H <sub>2</sub> to amount of		Ratio of amount of H <sub>2</sub> to mass of component in composition of mixture of	
		C <sub>2</sub> H <sub>5</sub> OH	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	CH <sub>3</sub> OH
1/1	500	0.00237	0.026	$3.7 \cdot 10^{-1/2}$	0.000520
	600	0.1341	0.148	0.002095	0.002960
	700	0.4448	0.480	0.00695	0.00960
2/1	500	0.0386	0.040	0.000471	0.000588
	600	0.2179	0.222	0.002657	0.003265
	700	0.7161	0.699	0.008733	0.010279
3/1	500	0.0528	0.054	0.000528	0.000628
	600	0.2959	0.292	0.002959	0.003395
	700	0.9593	0.897	0.009593	0.010430
5/1	500	0.0804	0.080	0.000591	0.000656
	600	0.4435	0.425	0.003261	0.003484
	700	1.3987	1.245	0.010285	0.010205

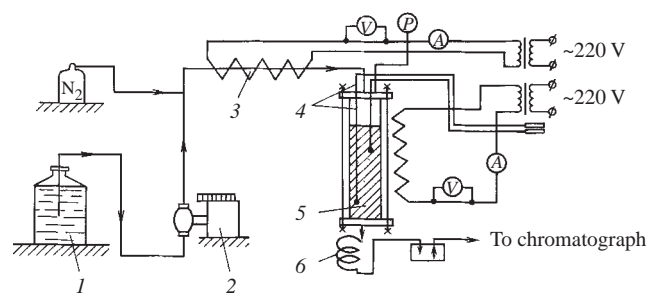


Fig. 1. Schematic diagram of experimental plant for alcohol reforming:  
 1) solution under investigation; 2) proportioning pump; 3) evaporator;  
 4) thermocouples; 5) reforming reactor; 6) refrigerator.

Eqs. (6) and (7) from discussion. Repeated analyses of thermodynamically equilibrium compositions of products of methanol reforming made it possible to determine the optimal ratios of methane to water for an initial mixture of reagents in the case of the simplified system. Table 2 compares hydrogen output on the basis of analysis of thermodynamically equilibrium compositions of products of alcohol reforming.

An experimental plant (Fig. 1), the basic subassembly of which is a thermochemical module – heterogeneous-catalytic reactor intended for the steam reforming of alcohol under atmospheric pressure – was developed for experimental investigation of the steam reforming of lower alcohols. The reagents were delivered to the reactor from a measuring tank via a proportioning pump. After mixing with a gas carrier (nitrogen), the reagents then proceeded into an electrically heated heat-exchanger/evaporator, in which the water–alcohol mixture was heated to the boiling point, and evaporated. Steam reforming of the mixture of reagents was carried out in the thermochemical module, after which the reaction products were delivered to a condenser coil to condense excess unreacted water vapor.

The reactor (Fig. 2) is built of an austenitic class of stainless steel, and is fitted with upper and lower flanged covers. The reaction mixture was fed through an inlet pipe. The reforming products were discharged through an outlet pipe. A fine-mesh metallic grid for containment of the catalyst is located on the lower cover. A heating coil positioned along the walls

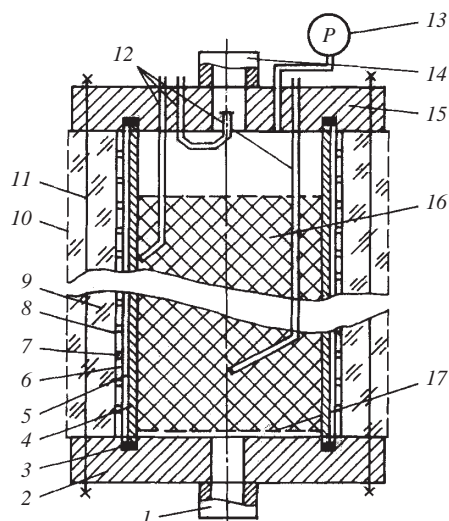


Fig. 2. Heterogeneous-catalytic reforming reactor: 1) outlet pipe (brass); 2) lower flange (stainless steel); 3) gasket (fluoroplastic); 4) reactor housing (stainless steel); 5) asbestos gasket; 6) electric insulation (mica); 7) electric heating element; 8) siliceous strip; 9) layer of kaolin felt; 10) fiberglass tape; 11) stay bolts with nuts; 12) thermocouples (chromel–alumel); 13) standard pressure gage; 14) inlet pipe (brass); 15) upper flange (stainless steel); 16) catalyst; 17) catalyst grate (mesh).

of the reactor is specified for high-temperature reactions. The body of the reactor is covered at the top by mica under the heating coil, and by asbestos between the coils, as well as by a siliceous strip, a layer of kaolin felt, and a fiberglass tape, respectively, above the heating coil for electric and thermal insulation.

A Chrom-5 gas chromatograph was used for chemical analysis of the reaction products. The analysis was performed in a tubular column filled with a Vitopol-B adsorbent (domestic analogy of the Porapak-Q column). A syringe was used to draw samples with a volume of 0.5 ml.

Granules of the solid Na-X zeolite carrier, which was impregnated with a copper–chromium–zinc–oxide composition, served as the catalyst.

In performing the experiments, the methanol content in the mixture amounted to 25, 40, and 55% (by volume). A further increase in methanol content was deemed inexpedient in connection with the formation of a condensed phase – carbon. It was established from the data obtained that hydrogen and carbon dioxide are, within the accuracy limits of the experiment, products of methanol reforming.

The degree of methanol reforming and the output of the desired product (hydrogen) were calculated for each solution investigated. For the analysis, the output of the product from reaction (5) was adopted as the maximum output.

As follows from the experimental data (Fig. 3), the output of hydrogen is observed to increase with increasing reactor temperature. The output of carbon dioxide conforms to a similar law. This corresponds to results of analysis of compositions in thermodynamic equilibrium in the reactions that take place during steam reforming of methanol.

The experimental data obtained suggest that methanol reforming approaches 100% in the catalytic system investigated. The output of hydrogen is also close to 100%. Due to the high hydrogen content in the samples, the chromatographic peaks for  $H_2$  and CO emerged not fully separated (the hydrogen peak overlapped the carbon monoxide peak), and, accordingly, the error generated in determining the CO was high, but its content did not exceed 2–3% (by volume). Only a negligible occurrence of condensed phase – carbon – was detected during visual inspection of the catalyst after reforming of a 55% solution of methanol (operating time of approximately 90 min). It can be concluded from this that a 55% (by volume) aqueous solution

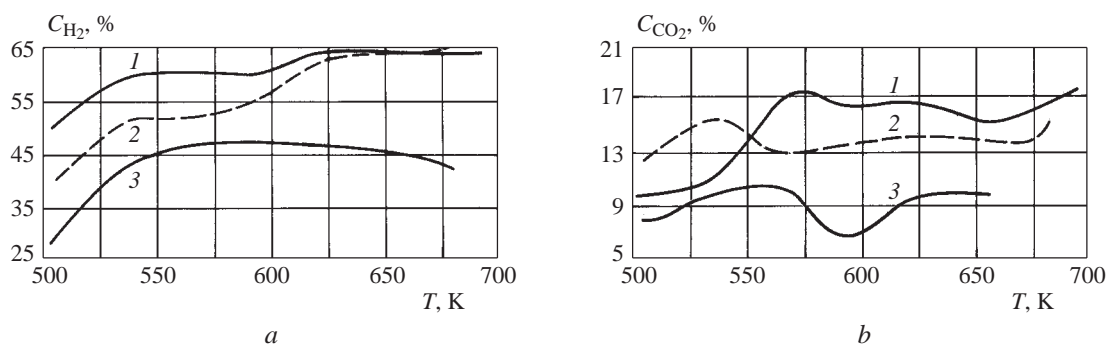


Fig. 3. Dependence of  $H_2$  (a) and  $CO_2$  (b) contents in sample on temperature  $T$  in reactor: 1) 55% of  $CH_3OH$ ; 2) 40% of  $CH_3OH$ ; 3) 25% of  $CH_3OH$ .

of methanol is optimal in terms of water content, and carbon formation for the  $Cu-ZnO-Cr_2O_3$  catalyst employed over the Na-X zeolite carrier. An additional loading experiment conducted at a constant  $300^\circ C$  indicated that the thermocatalytic module employed makes it possible to conduct stable steam reforming of methanol to a bulk rate of no lower than 450–500/h.

A separate experiment involving the steam reforming of ethanol yielded a negative result (carburization of the catalyst).

### Conclusions

1. It is expedient to use lower alcohols in steam-reforming reactions as a raw material for the production of hydrogen-containing gases.

2. Comparison of analytical results of thermodynamically equilibrium compositions of the steam-reforming products of methanol and ethanol demonstrated the advantage of methanol.

3. Concentration limits for formation of a condensed phase – carbon – are specified from results of thermodynamic calculations of the equilibrium compositions of the steam-reforming products of methanol, and it is established that carbon fails to form with increasing water content in the initial solution, which corresponds to a  $CH_3OH:H_2O$  ratio equal to 1:1.

4. A test plant was built to investigate catalytic processes in the continuous reactor on which the steam reforming of methanol and ethanol was investigated experimentally.

5. It is proposed that a copper–zinc–chromium oxide composition ( $Cu-ZnO-Cr_2O_3$ ) applied over Na-X zeolite, which was first investigated experimentally here, be used as a catalyst for the steam reforming of alcohols.

6. It was established experimentally that for the catalyst investigated there is no methane in the reaction products during the steam reforming of methanol within the limits of accuracy of the experiment. The products are hydrogen, carbon monoxide, and carbon dioxide.

7. Data on the ranges of effective concentrations of the water–alcohol mixture and process parameters for the steam-reforming reaction of methanol were obtained.

8. It is recommended that the catalyst investigated be used in a thermocatalytic module for the production of hydrogen-containing gases on-board a vehicle.

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